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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Paint Compositions and products Coated therewith

We, MINNESOTA MINING AND MANUFACTURING COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of 2501 Hudson Road, Saint Paul, Minnesota 55101, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to new paint compositions, methods of forming improved paint films, new finished non-tacky paint films, and structures having the paint films as a new part thereof. More particularly, the invention relates to new mobile compositions which may be applied as a paint-like film on a substrate and formed into a finished film state having an essentially glare-free flat and mark-resistant surface of tough non-abrading character. "Flat" as used herein means "optically flat"

These compositions are useful to form films on walls, ceilings, automobile dash-boards, office equipment, plastic and rubber articles (foamed or non-foamed), sheer materials or films (films containing vinyl-type resins, fabrics, paper), microporous sheets or articles (both natural and synthetic), and on a variety of other substrates where flatness as well as high resistance to unsightly marking is desired. Coated sheet material may be used as a wall covering or upholstery material, or in other ways. Coated embossible or formable metal sheet stock (usually marketed to converters in coiled condition) is useful in stamping and forming operations.

Mark-resistant characteristics for films of the invention, in combination with essentially glare-free flatness and a tough non-abrading character, are obtained by employing composi-

tions having a dispersed elastomeric particle phase and a mobile vehicle phase containing non-volatile ingredients to furnish an elastomeric matrix for the elastomeric particles in the final finished paint film. The elastomeric particles are non-coalescing. They are of a size of from 3 to 150 microns. They are dispersed in the mobile vehicle phase of the composition at a particle volume concentration (defined hereinafter) of 20 to 75%. At least 5% of the weight of the mobile vehicle phase is accounted for by non-volatile elastomer-film-forming organic material. Further, from 60 to 100% by weight of the total non-volatile material of the vehicle phase is non-volatile elastomer-film-forming organic material, and from 0 to 40% of the non-volatile material in the vehicle phase may be pigment. The elastomeric particles are insoluble in the vehicle phase. They also may contain 0 to 40% pigment by weight. The total volume of all particles equal to or greater than 3 microns in size in the composition plus the entire volume of any pigment particles dispersed in the vehicle phase (other than any of those pigment particles equal to or greater than 3 microns in size) accounts for no more than 85% of the total volume of non-volatile material in the composition.

Elastomeric particles and the elastomeric film-forming non-volatile ingredients of the vehicle phase both exhibit elastomeric properties in the final film; and this will be further described. Preferred compositions form films wherein the elastomeric characteristics of the particles and the non-volatile ingredients are relatively closely chemically related. Indeed, compositions useful to form the more highly mark-resistant films have elastomeric particles and non-volatile elastomeric film-forming ve-

hicle phase ingredients selected from the same chemical class or from related chemical classes.

5 The term "vehicle phase" as used herein is intended to include more than the ordinary meaning for that term as heretofore applied to paints. The term "vehicle," as well as "vehicle phase," refers to and includes all ingredients which are contained in particles having a size of less than 3 microns except those ingredients 10 which are contained in particles having a size of 3 microns or more. Thus, it includes suspended solid particles below 3 microns in size (including pigment of conventional size) in the liquid phase of the composition but not small pigment contained in the elastomeric solid particles which are dispersed in the vehicle phase. It includes volatile liquid that may be present in the composition (except that volatile liquid which may be within any micropores of elastomeric particles of 3 microns or more in the composition). It includes all organic film-forming binder ingredients dissolved or dispersed (as coalesceable droplets of the size well below 3 microns) in the volatile liquid 25 of the composition. It includes any thickeners or other ingredients which volatilize from an applied film or remain as part of the continuous matrix of an applied film (without which particles of 3 microns or more are bonded).

30 "Film-forming" and "elastomer-film-forming," as used herein with reference to organic material of the vehicle phase, refer to organic material which provides the elastomeric organic continuous matrix film for holding the elastomeric particles in position in the finished paint film. The organic material of the vehicle phase which performs this function may consist essentially of an admixture of precursor ingredients (whether soluble or dispersible in the volatile liquid of the vehicle phase) which interreact to form a resultant matrix film. It may be present as dispersed particles (of size well below 3 microns) coalesceable upon or after evaporation of volatiles to form the film. It may be present as dissolved solids which upon evaporation of volatiles provides the film. It may be such that formation of the film occurs under normal room-temperature conditions or is accomplished by fusion or compacting (without necessarily obliterating all micropores) of a mixture under elevated temperature conditions insufficient to destroy the essentially discrete elastomeric particulate.

55 Together with any pigments or other non-volatile ingredients of the vehicle phase, the film-forming organic material of the vehicle phase forms the composite binder matrix phase of an applied paint film of the invention. It is in this binder matrix phase (which may optionally be microporous) that the elastomeric particles are bonded in the finished paint film.

60 Non-coalescing elastomeric particles (whether solid or hollow or pore-containing) may vary from 3 microns in size up to 150 microns (minus 100 mesh U.S. Standard).

Particles of varied size within this range are employed in the composition of this invention. In most cases, at least 20 or 30% of the weight of the particles is accounted for by particles no greater than 90 microns. Particles above 150 microns are unsuitable for use in forming paint-type compositions. A negligible quantity (e.g., 5% by weight) of particles larger than 150 microns may be present in some compositions without untoward results. Generally, particles in excess of 150 microns are undesirable because they render paint application difficult. They also cause a problem in hiding underlying surfaces. Except in cases where spray paint application is contemplated, it is preferable from the standpoint of paint application (e.g. brush and roll application) to employ a mass of particles not exceeding about 90 microns in size. Usually they should not exceed about 75 microns in size with a major portion no larger than 40 microns in size.

Particles smaller than about 3 microns approach too closely the size of conventional pigment. When present at all, they are considered part of the vehicle phase of the compositions. They do not contribute to the velvet-type flatness for these paint films (which flatness is distinct from mere dulling caused by overloading with finely divided conventional pigment).

Most ideal results in terms of velvety flatness with freedom from glare and an essentially non-textured surface appearance, together with toughness and high mark-resistance, as well as painting ability with roll or brush application are gained by the use of elastomeric particles (particularly spheroidal elastomeric particles) between 3 and 50 microns in size. Very good results are gained when the particles are between 3 and 90 microns in size, with at least about 85% of the total particle weight accounted for by particles no larger than 75 microns and at least 50% of the total particle weight accounted for by particles no larger than 40 microns. Spheroidal particles (particularly those below 90 microns with most smaller than 75 or even 40 microns) are preferred over ground irregular particles. They form flat mark-resistant films which appear essentially non-textured and velvety.

As a generalisation, particles below 90 microns in size contribute to the formation of velvety flat films of essentially non-textured appearance when viewed with the naked eye. If several particles near 90 microns in size are present, the paint film does exhibit a textured appearance when viewed through a microscope, but the texture is not pronouncedly apparent under naked eye viewing. For textured appearance on naked eye viewing, elastomeric particles in excess of 90 microns up to about 150 microns are employed, preferably irregularly-shaped ground particles instead of spheroidal particles. And from the standpoint of gaining coverage with good hiding characteristics, at least about 20% of the weight of the

particles should be below 90 microns in size (even below 75 or 40 microns in size). Irregularly-shaped ground particles exhibit less tendency to roll about each other than spheroidal particles; thus, irregularly-shaped particles sometimes cause distinctive texturing which may be accounted for by the formation of some loose agglomerates of the particles (as present in the finished paint film), with elastomeric binder extending as a matrix between the particles in the agglomerates.

Where elastomeric particles of different colours are to be blended to gain a resulting colour appearing essentially uniform to the naked eye, the size of the admixed particles should be limited to no more than about 50 or possibly 60 microns. Mixtures of different coloured particles below about 25 microns give most ideal results. Admixed different coloured elastomeric particles, with at least about 0.1% by weight of particles of one colour (present in less amount than other colours) exceeding about 70 or 80 microns in size, gives a resulting attractive speckled appearance useful in some decorative applications.

The relationship between the total volume occupied by dispersed non-coalescing elastomeric particles and the total volume of non-volatile or solids material (both dispersed elastomeric particles and all of the non-volatile material of the vehicle phase) in these compositions is critical. Particle volume concentration (pvc) is a useful designation to express this relationship. It is a liquid displacement concept. A particle volume concentration of at least 20% (i.e., at least 20% of the total non-volatile material in the composition being elastomeric particles) is necessary in order to have a sufficient concentration of elastomeric particles to cause a multitude of small or minute "projections" on the exposed surface of the finished film, thus imparting visually-flat characteristics to the dried finished film of the composition. A particle volume concentration in excess of 75% causes the composition to be exceedingly difficult to handle as a paintable material to gain films which have their elastomeric particles firmly bonded. Generally, where the pvc is to be maintained below about 40%, it is preferred to employ elastomeric particles extending significantly into the larger sizes permitted (e.g., at least about 40% or even 75% by weight above 90 microns in size). Use of larger particles where low concentrations are employed insures the formation of small surface projections to at least some extent so that resulting flatness appearance from a light diffusing standpoint is gained for the finished film. In the case of smaller particles (e.g., 90 microns or less), the pvc is most desirably maintained at 40% or 50% or more in order to gain the most significant benefits of resulting flat paint film formation. At such higher pvc's, particles in the finished film tend to be piled up on one another, to an extent,

through the matrix of even the thinnest films; and they cause slight projections on the surface of the finished films.

It is generally true that the viscosity of mobile compositions for paint application should not exceed about 80,000 or 85,000 centipoises, but even higher viscosities may be employed under special industrial conditions. The viscosity is measured immediately after vigorous mixing so that the influence of interreaction of components and thixotropy is reduced to a minimum. Viscosities as low as 5 or 10 centipoises are satisfactory, though not preferred, in painting operations. Regardless of the presence or absence of pigment and other non-film-formers in the vehicle phase, at least 5% of the weight of that phase must be accounted for by non-volatile elastomer-film-forming organic material. If desired, the vehicle phase may be made up entirely of non-volatile monomeric or precursor ingredients reactable to form the non-volatile elastomer-film-forming organic material. In some cases, however, a quantity of non-volatile ingredients in the vehicle in excess of 80 or 90% of the weight of that phase may cause high viscosities (e.g., in excess of 80,000 or 85,000 centipoises) not usually preferred for painting operations. Such high viscosity compositions, when marketed, may be reduced in viscosity at the time of use by adding volatile diluents. Preferred paint compositions giving the described performance characteristics will usually contain volatiles in an amount accounting for at least about 20 or 30 weight percent of their vehicle phase. But the main essence of the invention is not per se dependent upon the presence or absence of volatiles in the vehicle phase of the paint.

Colouring matter (chromatic or achromatic-white, greys, and black as well as chromatic colours) may be omitted, but is preferably present in the composition either in the elastomeric particles or in the vehicle phase, or in both places. Without colouring pigment, the composition exhibits a transparent or translucent character which is somewhat frosty in appearance, particularly when viewed at high incident angles. Pigment in the elastomeric particles contributes greatly to the total hiding power of the composition, and causes improved colour appearance for painted film at a wide range of incident viewing angles. Thus, pigment in the particles is preferred. In a finished film, the light reflected from projecting particles is largely uniform in intensity at a wide range of viewing angles than is possible with respect to conventional flat pigmented films.

Any of a variety of known pigments may be employed. The quantity of pigment in elastomeric particles or in the vehicle phase must not upset the required parameters for the composition of these parts. In other respects, the quantity may be varied to suit one's desires. The quantity of pigment, whether organic or inorganic (such pigment generally being well

- below about 2 microns in size), in the elastomeric particles may vary from a fraction of a percent, or 0.1%, when used at all, up to about 40% of their weight. In the non-volatile material portion of the vehicle phase, pigment may be omitted, or be present from a fraction of a percent, or 0.1%, up to about 40% of the weight of that non-volatile material portion.
- Other additives such as thickeners and plasticisers may be incorporated in the solids material portion of the vehicle phase, or even in the elastomeric particles, provided elastomeric properties are maintained. If desired, small quantities of particles of rigid nature, such as for example glass or metal beads, above about 3 microns in size may also be added; but this is generally not preferred. When added, they are usually added in sizes varying from about 15 to 100 microns in diameter or even 150 microns in diameter. Preferably at least 50% or so of the weight of the addition of these rigid particles is accounted for by rigid particles which are at least as large, or larger, than 80 or 90% of the weight of elastomeric particles in a composition. In such cases, the added beads serve as islands distributed randomly in the finished paint film to bear the brunt of pressures applied over the film. This is particularly advantageous where it is desired to emboss or bend a sheet article comprising the finished film on a substrate sheet material. However, the volume of beads added should preferably not exceed about 25% of the vol-

ume of elastomeric particles in a composition. Further, the total volume of all particles above 3 microns in size in the composition, plus any dispersed pigment in the vehicle phase, should account for no more than 85% of the total volume of non-volatile material in the composition (e.g., at least 15% of the total volume of non-volatiles in the entire composition is organic elastomer-film-forming material).

Elastomeric particles tend to remain suspended in the compositions for longer periods than ordinary pigment particles. The density or specific gravity of the elastomeric particles is relatively less than that for normal inorganic pigment. It is therefore relatively closer to that for the vehicle phase. Specific gravity for elastomeric particles (even those containing pigment) is in general about 1.2 to 1.4 or 1.7. It is less than the specific gravity for most conventional inorganic pigments. Also, the specific gravity for the vehicle phase normally lies in the range of about 1.0 to 1.2 or even 1.4 or 1.7. It tends to the higher figures when no volatile liquid or only a small amount of volatile liquid is present and a fairly high pigment loading is used.

Several illustrative Examples of the invention will now be described.

EXAMPLE I

This composition is designed for paint-like application (e.g., brushing, rolling, and spraying) upon a substrate after mixing together Part A and Part B of the composition.

Ingredients	Parts by Weight in Pounds (Kilograms)	Solids Bulk- ing Volume Gallons per Pound (Litres per Kilogram)	Solids Gallon (Litre) Equivalent of Solids Weight
Part A			
Elastomeric particles	880. (39.8)	0.093 (0.159)	8.18 (6.34)
Xylol (volatile liquid)	40.0 (18.1)		
Cellosolve acetate (volatile liquid)	90.0 (40.8)		<
Elastomeric binder material precursor A (non-volatile reactant)	100.0 (45.3)	0.100 (0.171)	10.00 (7.77)
Part B			
Elastomeric binder material precursor B (non-volatile reactant)	6.7 (3.03)	0.118 (0.201)	0.79 (0.61)

Cellosolve is a registered Trade Mark.

- Weight in pounds (kilograms) times the solids bulking volume in gallons (litres) per pound (kilogram) gives the solids gallons (litres) equivalent of the weight of the non-volatile ingredients. The total solids gallons (litres) divided into the solids gallons (litres) for the elastomeric particles, times 100, gives the percent particle volume concentration for the composition.
- The pvc for this composition is 43.2%. Approximately 45.2% of the weight of the vehicle phase is accounted for by non-volatile film-forming elastomeric binder material precursor ingredients.
- Elastomeric particles for the composition may be either spheroidal or irregular (or angular) as obtained by grinding. Elastomeric particle preparation as such forms no part of the invention of this particular application. Suitable ground particles may be prepared by any known technique, as by grinding frozen elastomeric masses. Bead or dispersion polymerization techniques may be employed to produce spheroidal elastomeric particles (preferred for brush and roll paint application).
- Illustrative spheroidal elastomeric particles for this composition are polyurethane water-cured dispersed droplets of a melted (71° C) intimately blended mill base of 766.6 parts by weight of a waxy-solid isocyanate-terminated polyester prepolymer ("Multrathane F66" defined below), 24.8 parts by weight of chrome oxide pigment, and 33 parts by weight of phthalocyanine green pigment. The spherule particles are essentially free of pores and are dense. Essentially all of them are within the size range of 5 to 75 microns, with at least 50% of the weight thereof below 40 microns.
- The volatile liquids in the formula are solvents for the elastomeric binder material precursor materials. The elastomeric particles are insoluble in those liquids (but the elastomeric particles may optionally swell as a result of some liquid pick-up).
- Elastomeric binder material precursor A ("Multrathane F66") is a waxy-solid isocyanate terminated polyester prepolymer formed by reacting 4,4'-diphenyl methane diisocyanate with a polyester (i.e., the ester reaction between a glycol and dicarboxylic acid). It has an equivalent weight of 627 — 667 (i.e., its gram molecular weight per isocyanate group is 627—667). Approximately 6.3 to 6.7% of its weight is accounted for by isocyanate (NCO) groups.
- Elastomeric binder material precursor B is 1,4-butanediol. When this ingredient is blended with precursor A, a slow curing reaction between the materials takes place (e.g., approximately 48 hours at room temperature) to produce a polyurethane elastomer.
- When the vehicle phase ingredients of the formula are blended together and the viscosity promptly taken (using a Brookfield viscometer, 75° F, 60 rpm, No. 1 spindle), a reading of about 60 centipoises is obtained. The viscosity gradually increases because of the reactivity of the ingredients A and B. This formula illustrates that variable viscosities are possible for the vehicle phase. Also, in place of the vehicle phase specified one can use reactable monomeric-type ingredients which will react to give the desired vehicle phase with essentially no volatile solvent content.
- Where the formula is to be painted reasonably promptly (within about 4 hours) upon a substrate, all ingredients (both Part A and Part B ingredients) are mixed together with agitation for about 15 minutes. Also, where the mixture is to be stored or shipped under refrigerated conditions (e.g., between 35° F or 40° F) for only a week or so before use, it is suitable to mix all ingredients together prior to placing them in a sealed container for refrigerated storage and shipment. Usually, Part A is prepared separately, with violent agitation, to gain a uniform but random distribution of the elastomeric particles throughout the other ingredients (i.e., the vehicle phase) of Part A. Then Part A and Part B are placed in separate sealed containers for shipment. Shortly before paint application of the composition, the Part B ingredient is added and intimately blended with Part A as by stirring. Viscosity promptly after admixture is found to be about 475 centipoises (Brookfield, 75° F, 60 rpm, No. 2 spindle).
- Upon application of this composition as a paint film upon a substrate, the volatile liquids escape and gradual interreaction between the precursor ingredients takes place. The composition cures (by reaction between the precursor ingredients) to provide a tough protective attractive forest green coloured film which is visually-flat and highly resistant to marking. The finished film is velvety and appears uniformly flat to the naked eye. It is deformable, and recoverable from deformation. But since it is a mere paint film, its deformability and recoverability from deformation are not readily observable characteristics. Rubbing one's fingernail or a steel pointer over it does not leave a mark on it. Based upon several tests, it appears that the deformability and recoverability or restitution of the film largely accounts for its non-abrading characteristics and its high resistance to marking.
- EXAMPLE II**
- This formula is the same as Example I, except that the spheroidal elastomeric particles are replaced by ground elastomeric particles formed from a polyurethane elastomer mass. The polyurethane elastomer mass is the reaction product of the mill base for the illustrative spheroidal particles of Example I, mixed with about 51 grams of 1,4-butanediol (a curing reactant for the prepolymer of the mill base); and the reaction product is substantially cured. It is then frozen using solid carbon dioxide

and abraded using a belt sander of grit 80. Few, if any, particles below 3 microns in size are formed by this technique. Some particles may have web connections to others. Abraded particles are classified and those passed through a 100 mesh screen (150 microns) are used in the composition (although material passing 200 mesh (75 microns) is preferred). At least 80% of the weight of the mass passing 100 mesh is below 125 microns in size. About 15 or 20 weight percent of the particles of the mass is below 90 microns.

The composition of this example gives a resulting paint film (preferably formed by spraying) which is flat and mark-resistant and which

appears attractively textured to the naked eye.

The viscosity of the composition of this example (with the elastomeric particles present), as taken immediately after admixture of Part A and Part B ingredients, was 430 centipoises which was lower than that for Example I under identical conditions.

EXAMPLE III

The formula of this example illustrates a black paintable composition which may be marketed in a single container. The user may paint the composition directly from the container without need for pre-mixing separate parts.

Ingredients	Parts by Weight in Pounds (Kilograms)	Solids Bulk- ing Volume Gallons per Pound (Litres per Kilogram)	Solids Gallon (Litre) Equivalent of Solids Weight
Elastomeric particles (5 to 90 microns)	95.0 (43.0)	0.096 (0.164)	9.12 (7.05)
Wetting agent (sodium lauryl sulphate)	0.01 (0.0045)		
Water	51.0 (23.1)		
Water dispersion of elastomeric binder (46% solids by weight)	87.7 (39.6)	0.1044 (0.1785)	4.22 (3.26)
Water solution of thickener (5% by weight hydroxy- propylmethyl cellulose)	8.8 (3.98)	0.120 (0.205)	0.53 (0.04)
Water dispersion of pigment (25% by weight carbon black pigment less than a micron in size)	3.5 (1.58)	0.067 (0.114)	0.058 (0.045)

The pvc is 67.8%. Elastomeric particles plus pigment of the vehicle phase account for about 68.2% of the total volume of non-volatiles. Organic film-forming elastomer binder material accounts for 26.7% by weight of the vehicle. The total non-volatile vehicle accounts for 27.6% of that phase.

Elastomeric particles for this composition may be formed as described in Example II. Illustrative particles for this black composition may contain about 50 parts by weight of carbon black instead of the chrome oxide and phthalocyanine green pigmentation employed for the particles of Example II.

An illustrative water dispersion of binder is an aqueous dispersion of an acrylic copolymer of methyl methacrylate and ethyl acrylate. The copolymer contains about 60% by weight methyl methacrylate and 40% ethyl acrylate. A suitable copolymer dispersion ("Rhoplex

AC-33") contains about 46% by weight thermoplastic organic solids stably dispersed as minute droplets less than about 0.2 micron in size. This material satisfies the properties for the elastomeric binder.

To make the composition, first wet the elastomeric particles with the 51 parts of water and the wetting agent. The resulting slurry is mixed with a pre-blended mixture of the remaining ingredients of the formula using a high-speed high-shear mixer to grain blending. The final mixed composition exhibits a viscosity of about 1600 centipoises (Brookfield, 75° F, 60 rpm, No. 4 spindle). The vehicle phase of this composition exhibits a viscosity of about 350 centipoises (Brookfield, 75° F, 60 rpm, No. 2 spindle).

On painting (preferably by spraying) and drying, this composition provides a black, tough, elastomeric, mark-resistant, visually-flat

but textured surface film. Drying takes place by evaporation of the water. It is followed by gradual coalescence of the dispersed droplets of acrylic copolymer solids at room temperature into a finished unified continuous elastomeric matrix film.

EXAMPLE IV

An interesting plasticiser modified material which possesses the properties necessary for the elastomeric binder of the compositions hereof is plasticiser-modified polyvinyl chloride. An illustration of a composition of this type is:

Ingredients	Parts by Weight in Pounds (Kilograms)	Solids Bulk-ing Volume Gallons per Pound (Litres per Kilogram)	Solids Gallon (Litre) Equivalent of Solids Weight
Spheroid elastomeric particles from Example I	150 (68)	0.093 (0.159)	13.95 (10.81)
VM&P naphtha (volatile liquid)	12 (8.6)		
Diocetyl phthalate plasticizer	40 (18.5)	0.122 (0.208)	4.88 (3.86)
Polyvinyl chloride ("Geon 121")	66 (29.9)	0.086 (0.147)	5.67 (4.39)

Geon is a registered Trade Mark.

The pvc for this composition is 56.9%. It has a total solids content of 93.1%, and a non-volatile solids content accounting for 85% of the vehicle phase.

In formulating the composition of this Example, the polyvinyl chloride in finely-divided particle form (less than 2 microns particle size) is dispersed in the dioctyl phthalate plasticiser therefor by stirring. This forms a plastisol. Then the naphtha is added for dilution purposes. Finally, the elastomeric spheroids are mixed in by stirring (e.g., using a Waring blender).

The viscosity of this composition on formation is approximately 60,000 centipoises (Brookfield, 75° F, 6 rpm, No. 4 spindle). Its vehicle phase along exhibits a viscosity of about 85 centipoises (Brookfield, 75° F, 60 rpm, No. 2 spindle).

When coated as a paint film, the composition of this Example may not appear to provide an elastomeric finished film even after an extended time at room temperature. Nevertheless, the solids binder material of its vehicle phase possesses the necessary elastomeric requirements after the coated film is subjected to about 350° F for 15 minutes to cause homogeneous densification (e.g., fusion) of it. The heating causes the vehicle-phase mixture of or-

ganic film-forming ingredients to be converted to the finished film state possessing elastomeric properties. For compositions requiring heat to provide a finished film, it is practical to employ essentially fully-cured elastomeric particles (or at least elastomeric particles which do not melt or fuse under the heat treatment).

Excellent visually-flat and mark-resistant films of this composition may be formed on sheet stock capable of withstanding temperatures required for fusion or densification of the coating. Preferably, the composition is applied after a further reduction of viscosity by the addition of a few percent by weight of volatile ingredients. Metal sheet stock, when coated, is desirably pre-treated or primed with a priming film, as well known in the art. Factory controlled operation is possible. It is possible even knife coating may be used.

EXAMPLE V

The following illustrates a formula having a long pot life and one which is non-curing in the film state. It contains an elastomeric-film-forming binder material dissolved in a volatile liquid. The elastomeric-film-forming binder material component is in "elastomeric" condition while dissolved in the volatile liquid of the vehicle phase.

Ingredients	Parts by Weight in Pounds (Kilograms)	Solids Bulk-ing Volume Gallon per Pound (Litres per Kilogram)	Solids Gallon (Litre) Equivalent of Solids Weight
Elastomeric spheroids from from Example I	45 (20.4)	0.093 (0.159)	4.19 (3.28)
Cyclohexanone (volatile liquid)	270 (122.2)		
Elastomeric polyurethane	30 (13.6)	0.0996 (0.17)	2.985 (2.317)

The PVC of this composition is 58.5%. Its total solids content is 21.75% by weight. The elastomeric polyurethane accounts for approximately 10% by weight of the vehicle.

5 Suitable elastomeric polyurethanes ("Estane 5740X1") useful according to this example are substantially free of cross-links, and are essentially linear in character. They exhibit thermoplastic properties in addition to their other properties. They may be prepared as reaction products by heat reacting a mixture of (A) one mole of an essentially linear hydroxyl terminated polyester of a (1) saturated, aliphatic glycol having from 4 to 10 carbon atoms and having hydroxyl groups on its terminal carbon atoms and a (2) material selected from the group consisting of a dicarboxylic acid of the formula $\text{HOOC}-\text{R}-\text{COOH}$, where R is an alkylene radical containing from 2 to 8 carbon atoms and its anhydride, the polyester having an average molecular weight between 600 and 1200 and having an acid number less than 10, and (B) from about 1.1 to 3.1 moles of a diphenyl diisocyanate having an isocyanate group on each phenyl nucleus in the presence of (C) from about 0.1 to 2.1 moles of a saturated, aliphatic free glycol containing from 4 to 10 carbon atoms and having

hydroxyl groups on its terminal carbon atoms, the molar amount of the polyester and the free glycol combined being essentially equivalent to the molar amount of the diphenyl diisocyanate, whereby there are essentially no unreacted isocyanate and hydroxyl groups in the reaction product.

The composition of this Example may be applied by brush, roll or spray coating methods to give a forest green mark-resistant visually-flat velvety-appearing paint film. Drying in the nature of homogeneous densification takes place by evaporation of the cyclohexanone, which normally is relatively slow to evaporate from an applied paint film (e.g. several hours up to about 12 hours). If desired in industrial applications, heating of the applied film may be employed to drive out the solvent faster.

The total formula for this example exhibits a viscosity of about 900 centipoises (Brookfield, 75° F, 30 rpm, No. 2 spindle); whereas the vehicle phase of this composition exhibits a viscosity of 205 centipoises (Brookfield, 75° F, 60 rpm, No. 2 spindle).

In Table I, several properties for the elastomeric phases of the paint films formed using the formulations of the examples are set forth.

TABLE I

Example		Abrasion (Taber)	Hardness (Shore A-2)	Elonga- tion at break %	Tensile set at 45% Elongation	Coeffi- cient of resti- tution
I	E.P.	0.1	75	360	Less than 5%	25
	V.S.	0.1	80	500	Less than 5%	35
	V.B.S.	0.1	80	500	Less than 5%	35
II	E.P.	0.1	80	500	Less than 5%	30
	V.S.	0.1	80	500	Less than 5%	35
	V.B.S.	0.1	80	500	Less than 5%	35
III	E.P.	0.1	80	450	Less than 5%	25
	V.S.	0.6	90	500	Less than 5%	20
	V.B.S.	0.4	90	450	Less than 5%	15
IV	E.P.	0.1	75	360	Less than 5%	25
	V.S.	0.4	80	280	Less than 5%	10
	V.B.S.	0.4	80	280	Less than 5%	10
V	E.P.	0.1	75	360	Less than 5%	25
	V.S.	0.1	85	640	Less than 5%	25
	V.B.S.	0.1	85	640	Less than 5%	25

E.P. refers to the elastomeric particles (i.e., their composition) as they exist in a finished paint film.

V.S. refers to the composition of vehicle phase solids as that composition exists in a finished paint film.

V.B.S. refers to the vehicle-binder-solids composition, that is, the composition of the film-forming organic material (no pigment) of the vehicle phase, as that composition exists in a finished paint film.

The term "finished," as applied to paint films of the invention, refers to films essentially free of volatile liquid constituents and essentially free of bubbles, and which have undergone (1) curing of the film-forming organic binder material in the case of chemically-reactable vehicle mixtures, or (2) coalescence of dispersed coalesceable particles of film-forming organic binder material in the case of dispersed film-formers, or (3) homogeneous densification of dissolved (or dispersed) film-forming solids binder material (particularly in the case of non-reactable components), or (4) any combination of the foregoing. Finished films as "essentially free of bubbles" may contain a small amount of micropores. Or they may contain void spaces of microscopic character. But they do not contain larger voids of macroscopic character (i.e., visible with the naked eye when viewing cross sections through the film).

All test values in the table are obtained using thicker samples of the composition of the phases of the finished paint films than conventionally present in finished paint films. The

samples must be prepared so that they are essentially free of bubbles (macroscopic bubbles upset the reliability of test results). An excellent way of doing this so that the solvent of the composition does not cause macroscopic bubble formation is to allow a relatively long time (e.g., even a week in the case of thicker sections) to pass for solvent evaporation (and solvent evaporation may be aided by placing the sample in a chamber of reduced pressure). For solvent evaporation, the sample is preferably at room temperature or a temperature only slightly above (e.g. up to about 130° F. Further, when preparing samples, it is preferable to employ as little beginning solvent or volatile material in the composition as possible, while retaining good handling characteristics and blending of components. In finished paint films, bubble entrapment is not a significant problem since the films are so thin (e.g., a few microns up to 75, 100 or 150 microns). In the case of micropore-containing elastomeric phases, it is suitable to prepare thick samples for test purposes by being very meticulous

about slow solvent evaporation (even if curing is accomplished before solvent evaporation) so as to avoid macroscopic bubble formation.

The relationship between properties in the table and the performance of finished paint films is believed to be as follows. Abrasion resistance and elongation at break are indicators of toughness and resistance of a finished film to tearing and scuffing. Tensile set and the coefficient of restitution are indicators of deformability with sufficient recoverability after deformation to leave a finished film essentially unmarked by deformation. Hardness is an indicator of non-abrasive action by the major film phases themselves.

Abrasion (Taber) values were obtained using the rotary platform, double headed apparatus and method as described in ASTM D 1175. Specifically the apparatus used was Taber abraser Model 174 of Taber Instrument Company, North Tonawanda, New York, with H—18 abrading wheels and a 1000 gram load. The abrasion values listed are in grams of weight loss suffered by a specimen (1/8 inch thick and 4 inches in diameter) per 1000 cycles of planetary specimen rotation (70 revolutions per minute) in the Taber abraser. Elastomeric compositions for the invention exhibit less than 4 grams weight loss in this test, preferably less than 2 grams weight loss.

Hardness (Shore Durometer Hardness Type A—2) values are obtained according to ASTM D 1706—61. A type A—2 Shore indenter point is used. The values are maximum durometer values. Generally, elastomeric materials of the invention are not harder than a Shore Durometer of about 95. They have a hardness of at least 20 (otherwise the material is too soft to resist marks of identification and smearing). Preferably durometer readings are above 45. Values are set forth in the table in multiples of 5.

Elongation at break is obtained according to ASTM D—412—61T. The test procedure is conventional for determining the elongation at break of elastomer materials. Values are expressed in the percent that the specimen at rupture exceeds the original length of the specimen. Elastomeric materials for the invention have an elongation of at least 50%, and preferably at least about 75%.

Tensile set at 45% elongation is determined as follows. A specimen (about 1/8 inch square in cross section, with enlarged ends for gripping) is stretched to 145% of its original length and immediately released. After 10 minutes, the length of the specimen (not its enlarged ends) is measured. The excess of the second measurement of length over the original length, divided by the original length and multiplied by 100, gives the set in percent. For elastomeric materials of the invention, the set at 45% elongation is less than 10% and preferably less than 5%.

Coefficient of restitution values are in percent. They are derived by dividing the maximum height achieved by a rebounding plunger, by the original height of the plunger before dropping, and then multiplying the result by 100. Values were obtained using the resiliometer of the Precision Scientific Company; this device consists essentially of a level specimen-holding platform, a vertically mounted scale, a one ounce stainless steel plunger guided for free vertical drop and rebound (to and from a specimen) by a vertical stainless steel rod, and mechanical plunger release means. Specimens about 1 inch in diameter and 1/2 inch thick are subjected to test. The average of three readings were used for the values listed in Table I; and the result is listed in a whole number multiple of 5. Elastomeric materials of the invention exhibit coefficients of restitution at least above 5% and preferably above 10%.

This invention is not dependent upon any one chemical compound, since the properties of different compounds may be modified by blending ingredients therewith. For example, plasticisers may be added to an otherwise unsuitable chemical compound to convert it into a mass exhibiting the elastomeric properties for the invention. Also, new chemical compounds may be tailored to provide the elastomeric properties discussed.

WHAT WE CLAIM IS:—

1. A paint composition consisting essentially of a mobile vehicle phase (as herein defined) and non-coalescing elastomeric particles of 3 to 150 microns in size dispersed therein at a portable volume concentration (as herein defined) of 20 to 75%, at least 5% of the weight of the mobile vehicle phase being accounted for by non-volatile elastomer-film-forming organic material (as herein defined) with 60 to 100% by weight of the total non-volatile material of the vehicle phase being the elastomer-film-forming organic material and 0 to 40% being pigment, the elastomeric particles being insoluble in the vehicle phase and having 0 to 40% by weight pigment as a part thereof, the total of the entire volume of all particles equal to or greater than 3 microns in size in the composition, plus the entire volume of any pigment particles dispersed in the vehicle phase (other than any of those pigment particles equal to or greater than 3 microns in size) accounting for no more than 85% of the total volume of non-volatile material in the composition.

2. A composition as claimed in Claim 1 in which the non-coalescing elastomeric particles are smaller than 30 microns.

3. A composition as claimed in Claim 1 or Claim 2 in which the particle volume concentration (as herein defined) of the elastomeric particles is from 40 to 75%.

4. A composition as claimed in any preceding claim in which the non-volatile elastomer-film-forming organic material comprises a mixture of reactable precursor ingredients.
- 5 5. A composition as claimed in any of claims 1 to 3 in which the non-volatile elastomer-film-forming organic material comprises a film-forming mixture of non-volatile ingredients dispersed in a volatile liquid material.
- 10 6. A composition as claimed in any of claims 1 to 3 in which the non-volatile elastomer-film-forming organic material is dissolved in a volatile liquid material.
- 15 7. A composition as claimed in any of claims 1 to 3 in which the elastomer-film-forming organic material comprises a plastisol.
8. A composition as claimed in any preceding claim in which the elastomeric particles are spheroidal in shape.
- 20 9. A composition as claimed in any of claims 1 to 7, in which the elastomeric particles are irregularly-shaped ground particles.
10. A composition as claimed in any preceding claim in which the elastomeric particles have been made of polyurethane material.
- 25 11. A composition as claimed in any preceding claim having glass beads dispersed therein in a volumetric amount not in excess of one-fourth the volume of elastomeric particles present therein.
- 30 12. A paint composition according to Claim 1 and substantially as herein described in any Example.
13. An article comprising a substrate coated with a paint composition as claimed in any preceding claim.
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